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AND CERAMIC PROTECTIVE COATING SYSTEMS

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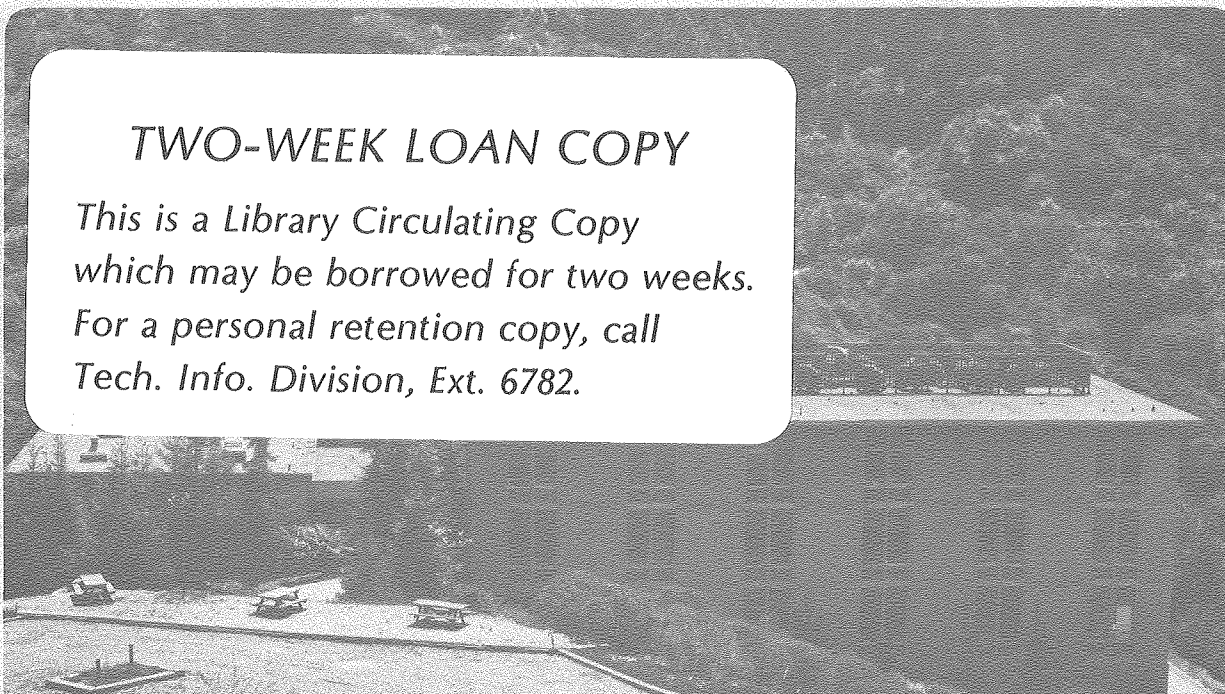
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## ADVANCED ELECTRON BEAM TECHNIQUES FOR METALLIC AND CERAMIC PROTECTIVE COATING SYSTEMS

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### BACKGROUND

A high priority at the Department of Energy is to ensure that directly fired heat engines in the U. S. currently operating on petroleum or natural gas make the earliest transition to the non-petroleum alternative fuels. High priorities are assigned to providing combustion zone durability with alternative fuel use in installed and current production gas turbine and diesel engines in an environmentally acceptable manner. Enhanced engine efficiencies operating on alternative fuels is also a priority concern. The engine operator interests are summarized as cost effective operation including the above priorities, fuel availabilities and cost, costs of engine modifications, fuel handling systems and maintenance. The early thrust is to determine the engine modifications and/or fuel handling systems necessary to operate with the more economical alternate fuel. For example, estimates to upgrade the SRC-II middle distillate-raw distillate fuel to the equivalent of No. 2 diesel fuel specifications could add \$10 to \$17/barrel. Thus economics suggest to first try to modify the engines rather than upgrade the fuel. Technically the approach will be to coevalue fuels and engine modifications.

The primary candidate alternative fuels are coal derived and oil shale derived in liquid or gaseous form. The Department of Energy is supporting development of four direct liquefaction coal derived fuels which are Exxon Donor Solvent, H-Coal, Solvent Refined Coal (SRC)-II and Two Stage liquefaction (TSL) via solid SCR-I. The SRC-II fuel is the only alternative fuel available in quantities sufficient for engine test and development. The SRC-II developer, Gulf, intends the raw distillate, SRC-II middle distillate as a diesel and gas turbine fuel. The

anticipated problems with this fuel stem from the low hydrogen carbon (H/C) ratio of about 0.75 and the high nitrogen level. High carbon fuels burn with a more luminous flame than petroleum,  $H/C \approx 2.0$ , fuel. This results in increased thermal radiation and combustion zone components with a view factor of the flame operating 60C hotter under equivalent conditions.

The increased thermal radiation is particular significant in the diesel engine using petroleum No. 2 fuel where exhaust valve surface temperatures operate just below the temperature threshold of aggressive hot-corrosion. Increased carbonaceous particulate and ash content in diesel engines increase erosion or wear in fuel pumps, injectors and cylinder liners.

In the gas turbine engine the higher carbon level presents an erosion problem on turbine airfoils, greater tendency for coking at the combustor which adversely affecting the combustion gas pattern and an increase in the incidence and severity of hot-streaking. Erosion has been shown in laboratory testing to have a synergistic effect with hot-corrosion which is markedly more severe than a summation of the independent effects (1).

Turbine airfoils used in industrial gas turbines have alloy compositions and processing treatments designed to accommodate the airfoil mechanical loadings encountered in engine thermal excursions. Unfortunately, these alloys meeting these strength requirements have often done so at the expense of corrosion/erosion resistance. Protective coatings optimized for hot-corrosion resistance must be added to the airfoil surface to extend component life. In addition, coatings are needed which reduce dependence on or consumption of critical elements such as cobalt and chromium.

Ceramic or thermal barrier coatings can provide particular attractive benefits for gas turbines and diesels. Ceramic coatings on gas turbine airfoils have the potential of dramatically improving corrosion/erosion resistance, turbine inlet temperatures or reduced airfoil cooling air requirements (2). The latter two could provide significant reductions in fuel usage. Also, ceramic or thermal barrier coatings provide major benefits on combustion chamber walls and transition ducts.

Ceramic coatings have already demonstrated significant benefits in diesel engines and have an exciting potential in the adiabatic diesel engine concept. Diesel engines used in marine propulsion and operating on residual fuels encountered significant hot-corrosion of exhaust valves and piston crowns after the 1973 fuel embargo. This was attributed to fuel processors extracting more higher quality fuels with resultant residual fuels having more contaminants. Also, considerably more coking was encountered which altered the fuel burning pattern resulting in higher temperatures of the exhaust valves and piston crowns. This diesel experience is different than the U. S. where fuel cost differentials in U. S. refinery practice did not justify operating with fuels of poorer quality than the light distillate No. 2 diesel or natural gas.

The Central Institute for Industrial Research in Oslo developed ceramic or thermal barrier coatings that increased exhaust valve and piston life by a factor of 2X to 3X in the marine propulsion diesels operating on low quality residual fuels. The adiabatic, or thermally insulated combustion zone, diesel engine holds great promise for diesel engine operation with higher efficiencies, extended durability and improved emissions. A turbo compounded adiabatic diesel having a specific fuel consumption (SFC) of about 0.28 lb fuel/HP Hr has been projected (3). This engine would require ceramic coatings, or monolithic ceramic parts, on exhaust and intake valves, injector tips, piston crowns, combustion chamber walls, cylinder liners and exhaust driven turbines. The Russians are coating piston crowns for truck diesel engines in production. They claim improved performance and easier cold weather starting. Another candidate for ceramic coatings are the precombustion chambers which can significantly reduce emissions, the biggest problem with diesels.

Successful ceramic coatings must withstand the stresses resulting from the thermal expansion mismatch and the stress and strain experienced by the substrate surface. Also, the ceramic coating must be impervious to corrosion condensates.

Candidate ceramic coatings use a metallic inner layer to act as a bond coat and a "fail safe" coating. Metallic coatings have provided an extension of gas turbine hot section life by a factor of 2 or more beyond that obtained with uncoated airfoils. Since industrial and utility gas

turbine engines will probably be operated with lower quality fuels in the near term, rather than make the transition to alternative fuels, metallic coatings will play a very important role in the near term to mid term. The most successful metallic coatings in gas turbines have been deposited by the PVD process. The genesis of both the metallic and ceramic coating technology is the aircraft gas turbine work for high temperature oxidation/corrosion protection. This high temperature coating technology provides the basis for improved capability of diesel and gas turbine engines to operate successfully on the most economic alternative fuels.

In the following sections the present status and understanding of protective coating types and processes will be reviewed together with a look at the future direction for improvements.

#### COATING REQUIREMENTS

The requirements for protective coating system are as varied as are the applications to which they are put. Some of the problem areas and concerns for gas turbines operating in various environments have been reviewed and summarized by G. W. Goward (4,5) and are presented in Table 1. Unfortunately, in other areas of energy conversion such as the diesel, it is presently impossible to construct a comparable table. This is in large part because of the insufficient level of understanding of the specific combustion zone environments, particularly with the as yet undefined synfuels, and their effect on materials of construction. In those systems using clean fuels operating in essentially uncontaminated environments, a philosophy of coating composition development has been established. These guidelines slightly modified and expanded are summarized in Table 2. The specifics of each of these items have been discussed in detail in the literature and studies continue to better understand the underlying factors.

It can be seen that a coating composition is selected which forms a protective oxide barrier layer. The specific oxide is often  $\text{Al}_2\text{O}_3$  but other oxides may show greater resistance to attack in more corrosive environments and are being actively explored. Oxide adherence is important and the use of so-called active elements to improve the

Table 1. Coating Degradation Modes for Various Gas Turbine Engines

	Aircraft					Industrial		Marine	
	Commercial			Military		Current	Future	Current	Future
	1960s	1970s	1980s	AF	Navy				
Conditions									
Oxidation	X	XX	XXX	XXX	X	X	X	X	X
Hot Corrosion	XX	X	X	X	XX	XXX	XXXX	XXXX	XXXXX
Thermal Fatigue	X	XX	XXX	XXX	X	X	X	X	XX
Erosion	-	-	-	-	-	(XX)	(XXX)	-	(XX)

Table 2. Some Requirements of High Temperature Protective Metallic Coating Compositions

1. Ability to form  $\text{Al}_2\text{O}_3$  (or other suitably stable and protective oxides).
2. Ability to form  $\text{Al}_2\text{O}_3$  over a wide compositional range thereby providing compositional freedom to optimize coating mechanical and physical properties.
3. Ability to promote oxide adherence; this provides increased lifetimes or comparable lifetimes at lower coating alloying content.
4. Freedom from detrimental elements and phases which can compete with the formation of the preferred protective oxide, or interact with the corroding product to promote protective oxide breakdown.
5. Freedom from detrimental elements and phases which can interact with the substrate to reduce its stability, load carrying ability and fatigue properties.
6. Presence of sufficient levels of beneficial "backup" elements to provide resistance to oxide breakdown and penetration, and to increase primary oxide element former activity.

adherence has been one of the more important developments in coating technology in the past 15 years. Coating structures and processing techniques to further augment and improve the active element effect are now being studied more intensely. Other beneficial and detrimental addition elements are being identified for specific uses and processes to include or exclude the appropriate ones developed. However, for all systems, the importance of compositional control of critical elements is apparent and this usually serves to establish the coating processing requirements.

The expansions of the use of protective coatings to other elevated temperature environments such as diesels and pressurized fluidized bed combustion system and the use of lower grade and alternate fuels such as the coal and shale derived synthetic fuels will add additional requirements to the selection of a suitable coating and process.



In particular the effects of metallic impurities and contaminants such as K, Na, Pb, V and the higher sulfur levels are predicted to accelerate presently identified degradation mechanisms if not introducing some additional ones. Table 3 compares the projected compositions of various blends of solvent refined fuels (SRC II) with present petroleum fuels. The specific level of the problem will only be known as the final blends are established and the resulting combustion products and their effects on materials determined. Active studies are in process to define the effects of the various types of levels of fuel. This information is necessary to establish the proper compromises between fuel types and blends and materials of construction for the advanced heat engines necessary to economically withstand the resulting combustion environment.

An additional factor which is becoming more important as the temperatures increase, and thermal gradients and stresses increase, particularly with the use of air cooling and thin wall airfoils, is the mechanical behavior of the coating and the effect of the coating and its application process on the mechanical behavior of the system. In some instances mechanical property considerations rather than environmental protectivity dictate coating composition and processing selection (6).

These and other requirements suggest that new coating compositions and protection strategies as well as new processing techniques to apply them may be required. It is therefore, of interest to now review the present status of coating application and processing techniques prior to the discussion of some advanced and future technology.

#### COATING PROCESSERS AND PROCESSING

Historically, discussions of coating compositions and degradation modes have usually been held independently of those of coating processing techniques and capabilities. This was in part because the coating processing requirements were rather simple, the substrates being coated were metallurgically simple, and they usually possessed some level of inherent surface stability. In most instances protection was provided by the formation of an  $Al_2O_3$  layer by an aluminum rich coating formed on and in conjunction with the substrate.

Table 3. Corrosive Metals Content in SRC-II

	Distillation Range F <sup>o</sup> (°C)	Cetane No.	Flash Point °F	Ash ppm	Na ppm	K ppm	Fe ppm	V %W	N %W	Viscosity 100 F <sup>o</sup> SUS
Middle Distillate	350-550°F (180-280°C)	<20	>160	8	0.01	0.01	3	<0.1	1.0	37
Heavy Distillate	550-950°F (280-480°C)	-	>180	500	3.70	5.00	100	<0.1 - 1.1	1.3	231-418
Blend 2.98 MD + 1 HD	-	-	>166	90	1.20	1.00	11	<0.1 - 1.0	1.1	- ∞
Petroleum No. 2 grade	370-650°F (188-338°C)	40-55	>130	24	0.50	-	-	<0.1	0.02	32.6-37.9
Petroleum No. 5 grade	-	-	>150	400	2-20	-	-	180	0.30	124-900

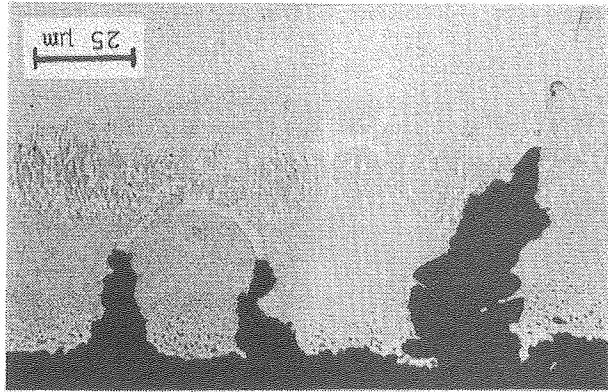
The most widely used coating system for turbine airfoils is the chemical vapor deposition (CVD) aluminizing process, either in the pack (pack aluminizing) or out of the pack. It was introduced in the late 1950s as the use temperatures and strength requirements of the second generation gas turbines necessitated the selection of lower chromium level superalloys.

The aluminizing process and the resulting structures are now well understood and explainable (7). It is important to note that this in-depth understanding is probably one reason for the widespread and successful use of these coatings and an equivalent level of understanding is necessary in the other coating technologies for their optimum utilization.

The structure of a typical three zone high activity (inward type) aluminide coating on a nickel base superalloy is shown in Figure 1 together with a list of some of its features and limitations. Because the coating depends upon the substrate for all elements but the aluminum, the composition and hence, properties of the coating depend, to a large extent, upon the particular alloy used. As the substrate alloys have been strengthened, and contain less chromium, more carbide and second phase reinforcement such as TaC or oxide dispersions, the quality of the coatings and their protectivity has decreased. Therefore, it is not surprising that the aluminides were not able to provide the required protectivity for advanced gas turbines being produced in the late 1960s, or for many commercial, marine and industrial turbines being produced in the 1970s. In addition to the limitation of inadequate protectivity, another problem with the aluminides arose with the use of thin walls and air cooling. High surface tensile strains produced by rapid cooling and cooling hole stress raisers resulted in early thermal fatigue cracking of these coatings. The NiAl, CoAl type aluminides have a high brittle-to-ductile transition temperature with corresponding low ductilities, less than 0.5 percent at the temperatures where maximum tensile stresses can occur (8). Premature cracking of critical airfoils can result. Attempts to lower the transition temperature by the reduction in coating aluminum content are limited by diffusional considerations and the required coating lifetime.

In the mid-1960s the ability to produce a coating tailored for the specific environmental and mechanical

### Aluminide Coatings



XBB 802-2597

#### Advantages

Simple Process  
Inexpensive  
Non line-of-sight  
Good oxidation resistance

#### Limitations

Substrate Composition and Process Limited  
Substrate structure limited  
Limited low temperature ductility  
Limited active element effect

Fig. 1. Microstructure of an inward type, three zone aluminide coating on a nickel base superalloy and advantages and limitations of the process. Note preferential oxidation of substrate carbides entrapped in outer zone.

conditions, essentially independent of the substrate composition and structure, was required. Attempts to modify the composition of the aluminide coatings by means of pre-surface treatment such as chromizing or noble metal plating have been partially successful for certain applications. However, because of limitations such as the solubility of chromium in the NiAl phase, the effect of a prior chromizing treatment on substrate stability and the limited ductility of the NiAl and noble metal intermetallic phase, for many applications, a more ductile and more totally substrate independent coating was still required. Such coatings have been termed the overlay type and depend for on the deposition process for their composition. Figure (2) shows the microstructure of an EB-PVD applied CoCrAlY overlay coating as presently used in production gas turbine engines.

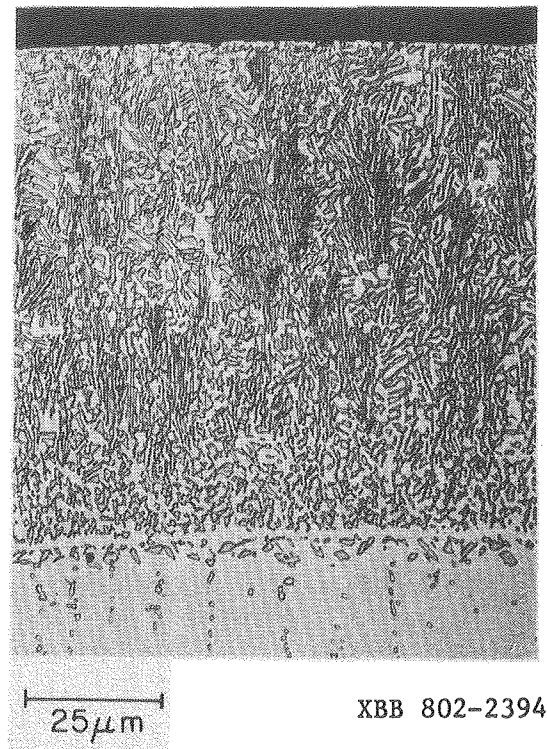


Fig. 2. Microstructure of EB-PVD applied CoCrAlY Coating showing minimum zone of coating-substrate interdiffusion.

Initially the overlays were metallic compositions but studies have shown that ceramic and thermal barrier coating and appropriate mixture of the two also showed great potential for particularly combustion zone components (9). The development and rationale for these latter types system is thoroughly covered by Levine et al in a following paper (10).

In the case of the metallic overlay coatings, a discussion of these compositions is a discussion of the MCrAlY (M = Fe, Co and/or Ni) coatings (5). Early interest focused on several cobalt base CoCrAlYs of relatively similar Cr, Al and Y levels and these have been the primary compositions used in production. The reasons for the selection of a specific composition has been discussed in the literature and involves as many considerations and trade-offs as occur in any materials selection procedure for a critical component such as a turbine airfoil. However, increasing demands have resulted in the need to develop additional compositions for more specific applications such as extended operation in a marine environment or

high temperature operation with high thermal fatigue strains on controlled solidification alloys in advanced military environments. Process improvements have also resulted in a tightening of the compositional range that can be specified and controlled. The result is that where one or two compositions were in use five years ago, today, over thirty production and experimental compositions are in use of under active development. It should however be cautioned that, as yet, many of these specific coatings are proprietary.

Some factors involved in the selection and level of the MCrAlY are elements and are briefly reviewed below.

Chromium is present primarily to provide oxidation and hot corrosion resistance. Because of the potential scarcity and cost, the trend is to use these critical elements in the small volume coating and not the larger volume substrate. Also, the potentially detrimental effects of higher chromium levels on mechanical properties of superalloys are not a concern in the essentially non-load carrying coatings. However, the use of too high a level in the coating could affect substrate stability. The presence of chromium also has the effect of increasing the aluminum activity of these coatings such that protective  $Al_2O_3$  can be formed at lower aluminum levels. This allows the use of coating compositions with lower aluminum contents and hence improved mechanical properties.

Aluminum is present to form  $Al_2O_3$  as previously discussed. While higher levels result in longer lifetimes, (at least under oxidizing conditions) excessive brittleness and a higher temperature brittle-to-ductile transition temperature can result. The trend is to use aluminum levels below 12 percent and coatings with a 5 - 10 percent aluminum range are presently being explored.

The key to the success of most overlay coating compositions is the presence (and possibly location) of an oxygen active element such as yttrium. In a manner not as yet completely defined, these elements promote adherence of the  $Al_2O_3$  layer during extended cyclic exposures, which results in an increase in coating protectivity at lower aluminum levels. The MCrAlY's with - 12 percent Al are significantly more protective than the aluminides with - 30 percent Al. The ductilities of the lower aluminum MCrAlY's are also a significant feature of the active elements containing coatings.

The continual demand for improvements in overlay coating performance has resulted in a number of coating development efforts being initiated during the past several years. It is predicted that the findings of these programs will result in the use of even more complex coating compositions and the introduction of structural as well as compositional control. The latter through the use of second phase particle additions.

Overlay coating processing techniques have had to expand to match the requirements of the coating compositions, structures and substrate geometries. The importance of coating processing procedures and techniques has increased to the point where processing rather than composition can be the factor limiting the introduction of an improved system.

#### OVERLAY COATING PROCESSING TECHNIQUES

As can be seen from the papers in this conference and from the recent publication in this area a variety of techniques are available for the application of coatings. It is not surprising, considering the importance of the problems, that many, if not all of these processes are being used or have been considered for the applications of protective materials. A number of the application techniques are presented in Table 4 and the list seems to increase with every review of the subject.

During the development of overlay composition and processes in the 1960's the electron beam evaporation physical vapor deposition (EB-PVD) process emerged as the most suitable, and a strong production technology has developed over the past 10 years. These developments resulted from the joint efforts of Pratt and Whitney Aircraft, East Hartford, CT and Airco Temescal in Berkeley, CA. Recent increases in the use of overlay coatings well as marine and land base propulsion and power generating turbines has accelerated the interest in overlay compositions and processing techniques, particularly sputtering and plasma spray. However, the EB-PVD process is presently the primary production technique and will be the basis for the following discussion.

TABLE 4. Potential Overlay Coating Application Processes

Physical Vapor Deposition

- (A) Electron Beam Evaporation and variations such as ion plating
- (B) Sputtering

Thermal Spraying

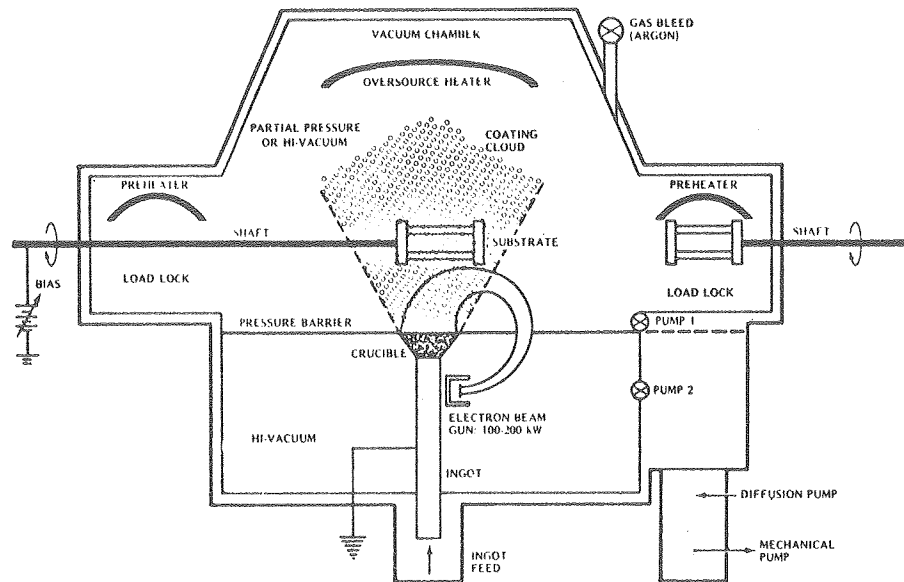
- (A) Plasma
- (B) Shielded Plasma
- (C) Low Pressure Plasma

Chemical Vapor DepositionFused Salt ElectrolysisLaser FusionSlurry Reactive Sintering

At present there are at least two suppliers of production EB-PVD airfoil coaters and while there are some significant design differences between them (which are not covered in this paper) the basic functions are essentially the same. Figure 3 is a schematic drawing of a multi load lock coater showing the basic components and features.

Like the gas turbine engine, the EB-PVD coater is simple in theory, but more complex in actual operation. In a suitable vacuum environment, generally  $10^{-4}$  to  $10^{-6}$  torr, an electron beam is impinged on a water-cooled copper hearth containing the material to be evaporated. A continuous ingot feeding system is used to maintain the molten pool height and composition at an equilibrium condition. Evaporation rate and coating thickness buildup are often monitored and controlled by a laser pool height indicator with suitable feedback to an ingot feed system. The shape and size of the ingot can vary, but is dictated primarily by present vacuum induction melting capabilities and the properties of these relatively high aluminum content coating alloys.





SCHEMATIC OF 200 kW COATER WITH GAS SCATTERING AND BIAS CAPABILITIES

XBL 803-8515

Fig. 3. Schematic representation of a two load lock EB-PVD airfoil coater showing relative location of key components and operations. Provisions for gas bleed and substrate biasing are also shown if required for 'ion plating'.

Due to the shape and distribution of the elements in the vapor cloud, the ingot composition can be different from the specified airfoil composition (11). In addition, the composition of the molten pool is different from both. However, under equilibrium conditions, which are rapidly established at pool temperatures of 1,600-1,900C, the average composition of the vapor out of the pool must be equal to the composition of the ingot being fed into the pool. The size and the shape of the crucible is selected to maximize deposition and thermal efficiency and, in many coaters, the shape and density of the electron beam is also controlled, producing a specific pool temperature profile with corresponding vapor composition and density distribution (12).

The EB power requirements vary with the coater size, the number of airfoils that can be properly positioned in the vapor cloud and the desired rate of coating deposition. Presently, coater power supplies are in the 100-200 KW range. While, early studies for other PVD systems indicated that increasing evaporation rates (which are proportional to deposition rates) resulted in a reduced quality coating structure, recent studies on MGrAlY airfoil coatings revealed the opposite. The quality of the deposited coating was found to increase as the evaporation/deposition rate was increased (13). Deposition rates exceeding 25  $\mu\text{m}/\text{min}$  are common.

Although in this paper and elsewhere most of the attention is directed towards the actual deposition of the overlay coating on a component such as an airfoil, a significant part of the process, time, expense and manpower expended can occur during the pre- and post-coating processing steps. A typical list of the processing sequence is shown in Table 5. As can be inferred, the actual coating deposition steps can be as little as 40-50% of the total coating cycle. Many of the individual steps are straight forward and are common to most other coating procedures. However, certain steps are critical and unique to the PVD process and some will be described in more detail below. A more detailed description of the process is presented elsewhere (14).

### Coating Deposition

The PVD coating of components differs in two significant ways from other coating processes and techniques. First, the substrate to be coated is preheated in vacuum to  $\sim 1000^\circ\text{C}$  prior to exposure to the coating vapor. During coating deposition, the substrate is maintained at temperature by a combination of pool radiation, heat of condensation and an additional over-source heater. The use of pre-heating and a heated substrate during coating results in the deposition of an adherent coating with some minimal amount of substrat-coating interdiffusion occurring during the coating cycle. The amount of interdiffusion during processing and service use once thought to be minimal has been recently found to be potentially significant (15). Depending upon the element and the processing technique used, this effect can have either a beneficial or detrimental effect. Coating spallation, a

Table 5. List of EB-PVD Processing Steps

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Receiving
Inspection and Batching
Surface Preparation:
Degreasing
Grit Blasting
Vapor Honing
Weighing
(if used as thickness and process control)
Loading into Fixtures and Masking
Coating Cycle
Pre-heat
Coating Deposition
Cooling
Removal from Fixtures
Re-weighing
Overspray Removal
Peening
Diffusion Heat-Treatment
(often substrate alloy solution treatment)
Aging Heat-Treatment
(if specified)
Inspection and Documentation
Shipment
Reworking--If Applicable
(stripping and re-cycling through appropriate process)

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problem with many coating processes and systems, is, thus, not a problem for properly cleaned substrates. In some EB-PVD coating work where argon gas is used to promote randomization of the essentially line-of-sight evaporation, sufficient cooling of the vapor can occur with the result that decreased structural quality and poor adherence is seen. For these conditions the use of a substrate bias, so-called ion-plating, can be used to provide the additional energy necessary for the required surface atom mobility and interdiffusion necessary for adherence and structural integrity (16).

A second feature of the EB-PVD overlay coating process is the rotation of the substrate during deposition. Coatings deposited on a rotated substrate often have an as-deposited columnar grain structure with unbonded interfaces known as "leaders." These structures have been shown to result from the shadowing by the individual grains growing in a preferred direction (17,18). Increasing deposition temperature which increases surface diffusivity reduces the density of these leaders, as does increasing the angle between the surface to be coated and the vapor flux (19).

#### Post-Coating Processing--Peening

It has been shown that a post-coating surface peening process (often using  $-200\text{ }\mu\text{m}$  glass beads) followed by a heat treatment results in a complete closure of these leaders and most EB-PVD applied coatings cycles including a peening operation. It could be noted that this peening operation also serves to remove chemical masking materials and to clean up areas of coating overspray. Peening has little affect on as-deposited surface smoothness, possibly some slight improvement to  $40\text{--}60\text{ }\mu\text{in}$ . Final coated airfoil surface smoothness is an important factor in turbine efficiency and could involve additional processing steps if as-deposited coatings were too rough.

#### Recoating

As for other coatings a procedure is necessary to allow removal of the overlay coating once applied. This need can result from the generally 1-5% coating rejects identified during inspection or from service operated parts returned for reworking and recoating. For these service parts, because of the expense of complex airfoils, it is desirable to remove the component prior to extensive attack of the substrate. The typical procedure involves the acid stripping of the coating, reworking the component and then recoating and subsequent return to service. Presently, a considerable research and development effort is being expended in studying airfoil repair and refurbishment techniques including effects of welding, and selected area replacement, hot isostatic pressing (HIP) and reheat treatment. This effort and the use of reworked parts is predicted to expand rapidly.

## NEW DIRECTIONS IN EB-PVD

As can be inferred from the proceeding discussion of coating requirements and the present status of overlay coating processing, additional understanding of the capabilities and limitation of the EB-PVD process is required. The results of some recent studies will be presented as examples of the present capabilities and as a guide to the direction of future work in this area.

## Improved Compositional Capabilities of Metallic Coating Production Using Single Source Evaporation

A factor often cited as limiting the wider use of EB deposition for alloy system is the implied inability of the process to evaporate elements with large differences in vapor pressures. In fact, the routine production deposition of protective overlay coating compositions of the MCrAlY type for gas turbine components indicates that there is actually a considerable latitude in the vapor pressure differences of elements that can be evaporated simultaneously from the single source.

Developers of coating compositions for improved oxidation, hot corrosion and thermal fatigue resistance under severe conditions are reporting the apparent benefits in coating lifetimes from the addition of small levels of certain elements, often with low vapor pressures, to systems forming protective oxides, such as MCrAlY systems which form  $Al_2O_3$

Suggested condition include those with high vapor pressures such as silicon and titanium and also those with much lower vapor pressures such as zirconium and hafnium. A study was initiated to determine the capability of single source EB-PVD to produce coatings containing their elements with widely varying vapor pressures (20). The following conclusions were made:

(1) In addition to yttrium, a number of other potentially useful additive elements with a broad range of vapor pressures can be simultaneously evaporated from a single source in a controlled manner in a MCrAl coating system.

(2) While these additions significantly change the equilibrium pool composition and temperature, the resulting evaporation parameters and power requirements are compatible with production EB evaporation procedures.

#### Improved Compositional Capabilities of Metallic Coating Production Using Dual Source Evaporation

The literature contains many references of the benefits to be gained through the use of graded coating compositions and/or structure with a corresponding transition in properties from the interface between the coating and the substrate, to the interface between the coating and the protective oxide and environment. For PVD type coatings, the use of multiple evaporation sources is one method of producing such gradients, and dual and triple source electron beam evaporation systems are available commercially.

In a DOE sponsored study, a dual source Gemini<sup>TM</sup> EB evaporation was used to demonstrate the feasibility of graded coating system (9).

For this study a Co-26%Cr matrix was used with aluminum as an example of a high vapor pressure addition element, and a Co26%Cr-10%Al-0.5% matrix was used with tantalum, as an example of a low vapor pressure addition element. Both elements were co-evaporated at varying rates to establish the processing concept and capability. Aluminum gradients ranging from 3-5% at the substrate interface to 10-15% at the surface of a 125  $\mu\text{m}$  (5 mil) coating were produced as well as larger gradients from 12% to 35% through a 75  $\mu\text{m}$  (3 mil) thickness. For the lower vapor pressure element, tantalum, a CoCrAl<sub>y</sub> coating composition was produced with a gradient ranging from 2-12%. Coatings with other combinations of matrix and graded addition elements could be produced using this technique.

Because of the potential beneficial effects of the presence of second phase particles in coatings (improved oxide adherence effects, greater active element stability, improved mechanical properties both at elevated and lower temperature, etc) a preliminary evaluation of the separate but simultaneous evaporations of a ceramic such as Al<sub>2</sub>O<sub>3</sub> or stabilized ZrO<sub>2</sub> and a CoCrAl<sub>y</sub> was conducted. It was established that such two phase ceramic/metal coating systems could be produced using techniques established in this program.

Further advances in this processing area awaits the input of coating developers and users.

#### Structural and Compositional Capability of Ceramic Coating Production Using Single Source Evaporation

In the search for new materials for use at high temperatures in gas turbine engines, probably one of the areas of greatest interest and activity has been in the effort to use ceramic materials structurally and possibly of greater recent interest, as a protective and thermal barrier coating. Several excellent reviews of the present status of these various efforts are available (2,10) and will be covered in a following paper in the proceedings of this conference. In these studies of ceramic coatings, it is seen that a number of ceramic compositions and fabrication processes are under active development. However, from the initial results, it is apparent that for ceramic coating, the method of deposition and the resulting structures can be as important as the compositions themselves, particularly in influencing the mechanical behavior.

The EB-PVD process has been used for many years in the production of ceramic coatings (e.g.,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ) for the electrical and optical industry, albeit, for the deposition of relatively thin layers. A large production technology has been established in this area. The availability of the large units such as the 100-200 KW metallic airfoil coaters suggested the re-evaluation of the EB-PVD process for the deposition of thick ceramic coatings.

A study was therefore initiated to determine whether this EB-PVD state-of-the-art technology for metallic coatings could be combined with the EB-PVD state-of-the-art for thin ceramic coatings to produce useful thick (25-250  $\mu\text{m}$ ) ceramic layers (21).

Initial experiments in one crucible of a dual source system, re-established that several ceramics including  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  materials could be deposited. The form of the ceramic feed stock was found to be important although both rod and chunk materials were successfully evaporated. The remaining experiments were conducted in a 100 KW coating unit, as might be used in production, and a fully stabilized 12%  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  ceramic was used for the results reported here.

Evaporation studies in high vacuum ( $10^{-5}$  torr) produced a dark gray coating, obviously hypostoichiometric with respect to oxygen. (At this early point of the program, no efforts were made to establish composition). Two studies were initiated, one to evaluate the effects of evaporation in a partial oxygen pressure and the other to study the effects of various coating processing parameters on relative composition and structure.

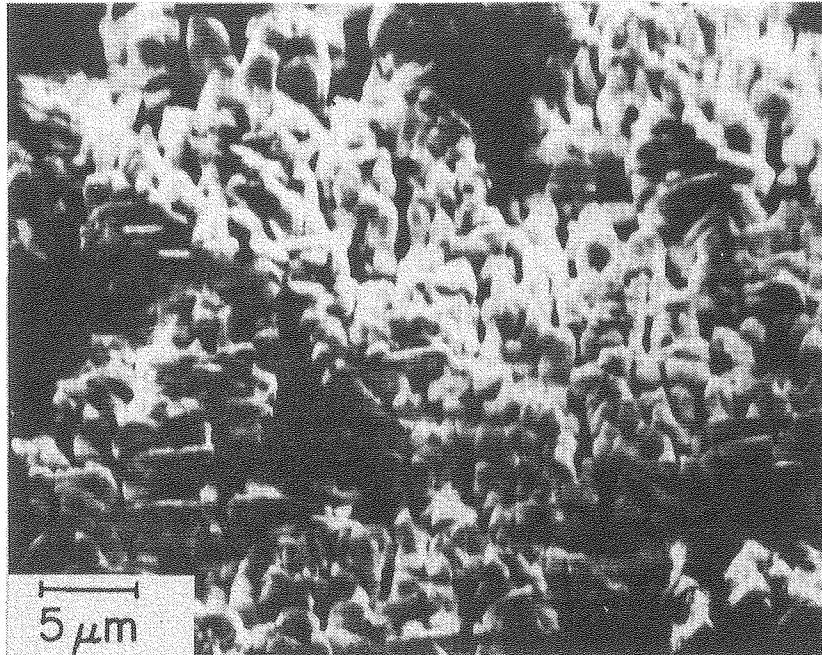
In the evaluation of the effects of varying oxygen pressure and the method of its introduction into the vacuum chamber, it was established that through the use of suitable electron beam gun baffling and injection location, a "white" zirconia coating in thickness from 25  $\mu$ m to over 250  $\mu$ m could be produced. Although the degree of stoichiometry was not determined, subsequent heat treatment, in air, resulted in little weight change indicating an as-deposited composition close to stoichiometry.

In the structural study, the effect of substrate rotation was evaluated (as previously noted, substrate rotation is used in the production of metallic EB-PVD coatings and results in the growth of a columnar grain structure) (17,18). A coating on a stationary plate produced a relatively dense coating with just the remnants of growth cones as might be expected for metallic coatings deposited at 1000°C. However, rotation of the coating sample tab resulted in the growth of a columnar grained, leader type, zirconia structure similar to that produced in the deposition of metallic coatings under comparable conditions of deposition rate and temperature (Figure 4). Preliminary SEM structural evaluation indicated that these columnar ceramic structures were approximately four times finer than for a similar as-deposited CoCrAlY structure.

Because of the considerable interest in ceramic materials with segmented structures with their potential ability to withstand larger thermally induced interfacial stresses without spallation, the demonstrated ability to produce these structures and the potential to modify their grain size and density using standard EB-PVD processing techniques was considered very significant.

Further studies are planned to expand this study to better characterize the range of structural variations possible with the EB-PVD deposition technique and to evaluate the effects of other ceramic compositions on the





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Fig. 4. SEM microstructure of EB-PVD applied Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> coating showing the segmented growth structure possible with this process.

processing parameters. Specimens of appropriate structure and composition will be made available for corrosion and mechanical property evaluation programs.

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## SUMMARY

The needs for the use of protective coatings will continue to increase as our quest for greater energy efficiency and more diversified fuel sources expand. Overlay coatings and composite system will be required to meet these requirements in a cost effective manner consistent with materials availability. These needs have spurred interest and activity in the overlay coating processing area in general and in EB-PVD techniques in particular where even greater activity is predicted in the future.

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